

foreign supplier of barium carbonate to the U.S. market. A new source is China, and this country may become a major supplier in the future. Domestic production in 1980 was 2×10^6 t and imports were 1.7×10^6 t.

USES.²⁵ The applications of barium compounds are varied and important. Each year over 3×10^6 t of barite is consumed. Over 90 percent is used for oil drilling muds. *Barium carbonate* is sometimes employed as a neutralizing agent for sulfuric acid and, because both barium carbonate and barium sulfate are insoluble, no contaminating barium ions are introduced. The foregoing application is found in the synthetic dyestuff industry. The glass industry uses 28 percent of the barium carbonate produced, and brick and clay producers, 33 percent. When barium carbonate is added to the clay used in making bricks, it immobilizes the calcium sulfate and prevents it from migrating to the surface of the bricks and producing a whitish surface discoloration. Miscellaneous uses include TV picture tubes and as a flux for ceramics. Witherite is used chiefly to prepare other compounds. *Barium sulfate* is a useful white pigment (Chap. 24), particularly in the precipitated form, blanc fixe. It is used as a filler for paper, rubber, linoleum, and oilcloth. Because of its opacity to x-rays, barium sulfate, in a purified form, is important in contour photographs of the digestive tract. The paint industry is the largest single consumer of barium compounds. Barium sulfide and zinc sulfate solutions are mixed to give a precipitate of barium sulfate and zinc sulfide, which is given a heat treatment to yield the cheap but good pigment *lithopone*, as described in Chap. 24. Barium chlorate and nitrate are used in pyrotechnics to impart a green flame. Barium chloride is applied where a soluble barium compound is needed. Barium saccharate is used by a large beet-sugar company in recovering sugar from discarded molasses (Chap. 30).

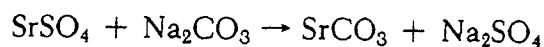
MANUFACTURE. The preparation of soluble barium salts is simple where witherite is available. The only steps necessary are treatment with the proper acid, filtration to remove insoluble impurities, and crystallization of the salt. Since there is little witherite in the United States, barium salts are prepared from barite. The high-temperature reduction of barium sulfate with coke yields the water-soluble barium sulfide, which is subsequently leached out. The treatment of barium sulfide with the proper chemical yields the desired barium salt. Purification of the product is complicated by the impurities introduced in the coke. Pure barium carbonate and barium sulfate are made by precipitation from solutions of water-soluble barium salts. Much barite is ground, acid-washed, lixiviated, and dried to produce a cheap pigment or paper or rubber filler, or changed to blanc fixe.

STRONTIUM SALTS

Uses of strontium salts are small with respect to tonnage consumed but they are important; they include red-flame pyrotechnic compositions, such as truck signal flares and railroad "fusees," tracer bullets, military signal flares, and ceramic permanent magnets. Strontium carbonate is widely used as an x-ray screening agent in television picture-tube face plate glass and has no commercial alternative. Low-grade strontium deposits are available in this country, but are not currently in use; high-grade celestite is imported from Mexico and the United

²⁵*Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981 p. 103; *Chem. Week* 129 (6) 26 (1981).

Kingdom. This ore (strontium sulfate) is finely ground and converted to the carbonate by boiling with 10% sodium carbonate solution, giving almost a quantitative yield:



From reaction of the strontium carbonate with appropriate acids, the various salts result.

LITHIUM SALTS

During World War II lithium hydride was reacted with seawater to produce a convenient lightweight source of hydrogen for the inflation of air-sea rescue equipment. Interest in lithium compounds grew from 1954 to 1960, when the Atomic Energy Commission (AEC) bought vast quantities of lithium hydroxide, presumably for use in the production of hydrogen bombs.²⁶ Termination of these contracts left a substantial excess, which in turn has fostered new commercial uses. The largest known lithium ore reserve in the world is in the King's Mountain district of North Carolina. Currently a large part of the free world's output of lithium oxide comes from this source as spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$). There are only two producers of lithium and lithium salts in the United States: Foote Mineral Co. and Lithium Corp. of America. Foote produces lithium from the ore in North Carolina and from subsurface brines in Nevada. All of Lithium Corp. production is from North Carolina sources. In 1980 the U.S. produced 6480 t of lithium metal equivalent and exported 33 percent of the total.²⁷

USES. Lithium carbonate, the most widely used of the compounds, is employed in the production of lithium metal and frits and enamels. Together with lithium fluoride, it serves as an additive for cryolite in the electrolytic pot line production of primary aluminum. The addition of 2.5 to 3.5% of lithium carbonate to the electrolytic bath causes the formation of a eutectic mixture that lowers the bath temperature, power consumption, and rate of volatilization of fluoride salts. This use accounts for 33 percent of the lithium produced in the United States.²⁸ Lithium-base greases, often the stearate, are a large outlet. These lubricants are efficient over the extremely wide temperature range -51° to 160°C . Lithium hydroxide is a component of the electrolyte in alkaline storage batteries and is employed in the removal of carbon dioxide in submarines and space capsules. Lithium bromide brine is used for air conditioning and dehumidification. The hypochlorite is a dry bleach used in commercial and home laundries. Lithium chloride is in demand for low-temperature batteries and for aluminum brazing. Other lithium-compound uses include catalysts, glass manufacture, and of course nuclear energy. A newer use for lithium carbonate is as a drug to treat manic depression. The Food and Drug Administration (FDA) approved its use for treating mind disorders in 1970.²⁹

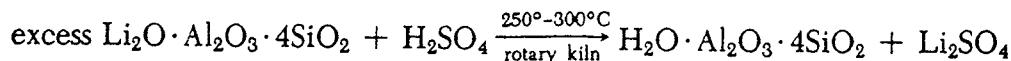
²⁶The lithium hydroxide for sale by AEC is devoid of lithium-6 isotope.

²⁷ECT, 3d ed., vol. 14, 1981, p. 450; *Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 519.

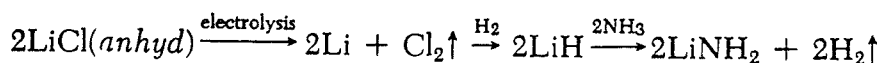
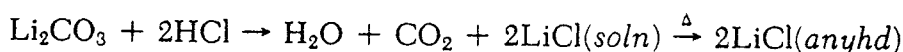
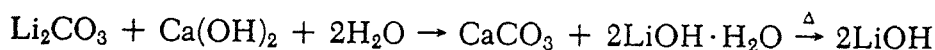
²⁸Stinson, Lithium Producers Gear Up for Bright Future, *Chem. Eng. News* 59 (43) 11 (1981); *Chem. Eng. News* 59 (42) 10 (1981); *Chem. Week* 128 (10) 19 (1981).

²⁹*Chem. Week* 110 (10) 41 (1972).

MANUFACTURE. Since spodumene is by far the most important ore, the manufacture of lithium carbonate from it is presented. Spodumene ore (beneficiated to 3 to 5% Li_2O) is converted from the alpha form to the beta form by heating to over 1000°C . The alpha form is not attacked by hot H_2SO_4 . The beta form is treated as follows:



The water-soluble lithium sulfate is leached out and reacted with sodium carbonate to yield lithium carbonate. Various salts are derived from the carbonate as follows:



BORON COMPOUNDS

The important naturally occurring ores of boron have been colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), tincal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), and boracite ($2\text{Mg}_3\text{B}_6\text{O}_{15} \cdot \text{MgCl}_2$). However, boron-containing brines and kernite, or rasorite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), are also sources in the United States.

USES. Borax (tincal), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is the most important industrial compound of boron. Table 5.2 lists the U.S. consumption of boron minerals and compounds. The largest single use is in the manufacture of glass-fiber insulation. Boric acid (H_3BO_3) is a weak acid that finds some use in the manufacture of glazes and enamels for pottery. Its main uses are as a fire

Table 5.2 U.S. Consumption of Boron Minerals and Compounds (metric tons of boron oxide content)

End Use	1980	1981
Glass-fiber insulation	81,265	94,082
Fire retardants		
Cellulosic insulation	45,632	31,179
Other	1,182	2,545
Textile grade glass fibers	45,814	52,268
Borosilicate glasses	40,732	40,000
Soaps and detergents	24,179	26,452
Enamels, frits, glazes	12,090	10,635
Agriculture	14,271	15,090
Metallurgy	6,000	6,182
Nuclear applications	454	364
Miscellaneous uses	43,905	23,090
Sold to distributors, end use unknown	33,540	36,815
Total consumption*	349,000	338,780

* Data may not add to totals shown because of independent rounding.

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982,

retardant for cellulosic insulation and in the manufacture of borosilicate glasses and textile-grade glass fibers

MANUFACTURE. All of the domestic boron ores and brines that are used commercially in producing boron compounds are in California. Three-quarters of the borates thus produced are from an open pit mine in Kern county. Crude and refined hydrated sodium borates and hydrous boric acid are produced by U.S. Borax and Chemicals Corp. from kernite and tincal mined at Boron, Calif. A new plant (1980) at Boron produces 180,000 t/year of boric acid from kernite. The ore is crushed and blended to a constant B_2O_3 content. The blended ore is fed to the dissolving plant and mixed with hot recycle liquor. Liquor and fine insolubles are fed to a primary thickener. There are four thickener stages operating countercurrently. The strong liquors are crystallized in a continuous vacuum crystallizer.³⁰

Kerr-McGee Chemical Corp. uses a process that involves the use of an organic solvent to extract the borax from the Searles Lake brines.³¹ See Figs. 2.1 and 2.2.

The boric acid is extracted with kerosene, carrying a patented chelating agent not yet disclosed but probably an aliphatic medium chain length polyol, in a mixer-settler system. In a second mixer-settler system, dilute sulfuric acid strips the borates from the chelate. The aqueous phase with boric acid, potassium sulfate, and sodium sulfate is purified by carbon treatment and evaporated in two evaporator-crystallizers; from the first, pure boric acid is separated, and from the other, a mixture of sodium and potassium sulfates.

RARE-EARTH COMPOUNDS

Chemical elements with atomic number 58 to 71 are so nearly identical in properties that they are separated only with difficulty and are called as a group *rare earths*.³² The name is a misnomer, since they are neither rare nor earths. Compounds of lanthanum, yttrium, and scandium are often included in this group, as are the actinide rare earths (elements 89 and above). Cerium and thorium are the most important commercially. Although rare earths occur in certain minerals native to the Carolinas, these minerals have not been able to compete with the richer monazite sands found in Brazil and in Travancore-Cochin, India. Preliminary separation is accomplished by the use of jigging, in this case the valuable material is denser than the worthless fraction. The concentrates are leached with hot sulfuric acid of strength greater than 66°Bé, and the rare-earth metal compounds are precipitated by dilution of the sulfuric acid solution. Lanthanum and cerium are separated by fractional crystallization, and the others are separated by liquid-liquid extraction or ion-exchange processes.

Molycorp, Inc. has developed a solvent extraction process for the production of the oxides of lanthanum, cerium, gadolinium, terbium, praeosodymium, neodymium, yttrium, and europium in tonnage quantities. The ore, bastnäsite, mined in California, is concentrated by hot-froth flotation and then subjected to solvent extraction.³³

³⁰*Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 133.

³¹ECT, 3d ed., vol. 4, 1978, p. 67; Shreve, *Organic and Other Non-aqueous Solvents as Processing Media for Making Inorganic Chemicals*, *Ind. Eng. Chem.* 49 836 (1957).

³²*McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 11, McGraw-Hill, New York, 1982, p. 401.

³³*Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 669.

The glass industry is the largest consumer of rare-earth compounds, mostly as oxides for rapid polishing of plate glass, as well as precision optical equipment and eyeglasses. Yttrium and europium oxides are used in ton quantities as phosphors for TV screens. Lesser quantities of compounds are used for coloring, decoloring, and opacifying glass. Other uses are in ultra-violet absorbing glass, in certain high-lead glass with increased radiation stability, in color television tubes, lasers, and x-ray intensifying screens. Fluorides and oxides are consumed in the production of carbon electrodes for arc lighting of high intensity and good color balance. Over 300 t of the rare-earth silicide, known as *misch metal*, was used in high-strength, low-alloy steels in 1980. Thorium is of interest in nuclear reactions.

SODIUM DICHROMATE

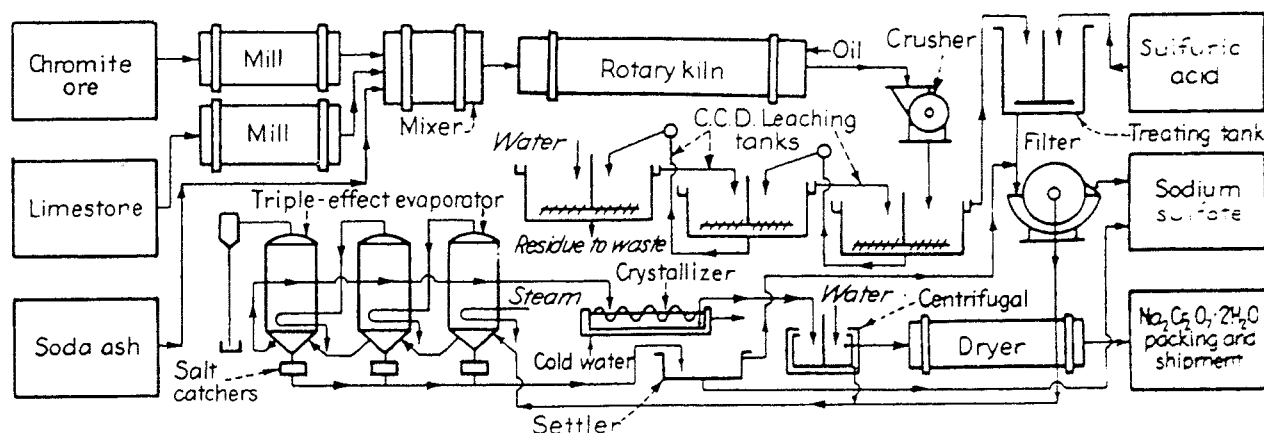
The starting material for the manufacture of sodium dichromate and other chromium compounds is chromite, a chromium iron oxide containing approximately 50% Cr_2O_3 , the balance being principally FeO , Al_2O_3 , SiO_2 , and MgO . There are no high-grade chromite deposits in the United States, and most of the ore used in the chemical industry is imported from the U.S.S.R. Much sodium dichromate is consumed as the starting material for making, by glucose reduction, the solutions of chromium salts employed in chrome leather tanning (Chap. 25) and in chrome mordant dyeing of wool cloth. Certain pigments, such as yellow lead chromate, are manufactured basically from sodium dichromate, as are also green chromium oxides for ceramic pigments. Over half of the chromium enters the metal field as stainless steel and other high-chromium alloys and for chromium plating of other metals, the balance being about equally divided between chrome refractories and chrome chemicals.

The ore is ground to 200-mesh, mixed with ground limestone and soda ash, and roasted at approximately 1200°C in a strongly oxidizing atmosphere. The sintered mass is crushed and leached with hot water to separate the soluble sodium chromate. The solution is treated with enough sulfuric acid to convert the chromate to dichromate, with the resulting formation of sodium sulfate. Most of the sodium sulfate crystallizes in the anhydrous state from the boiling-hot solution during acidification, and the remainder drops out in the evaporators on concentrating the dichromate solution. From the evaporator the hot, saturated dichromate solution is fed to the crystallizer, and then to the centrifuge and dryer (Fig. 5.7).

HYDROGEN PEROXIDE

Hydrogen peroxide is the most widely used peroxide compound. Originally, it was produced by the reaction of barium peroxide and sulfuric acid for use as an antiseptic, but this process and use have been superseded.

USES. Hydrogen peroxide applications include commercial bleaching dye oxidation, the manufacture of organic and peroxide chemicals, and power generation. Bleaching outlets consume more than one-half of the hydrogen peroxide produced. These include bleaching of wood, textile-mill bleaching of practically all wood and cellulosic fibers, as well as of major quantities of synthetics, and paper- and pulp-mill bleaching of groundwood and chemical pulps. The advantage of hydrogen peroxide in bleaching is that it leaves no residue and gen-



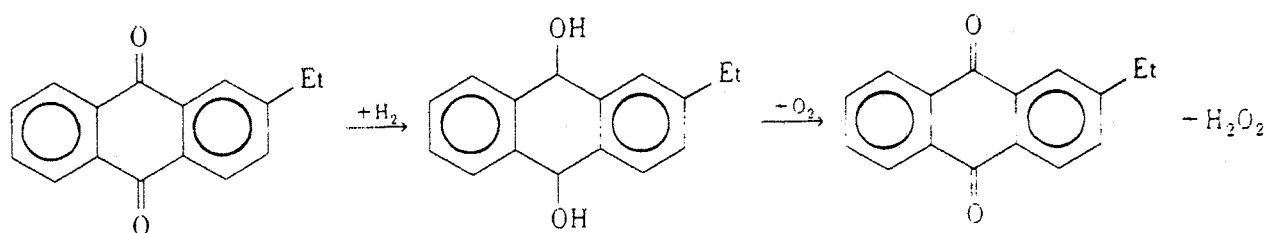
In order to produce 1 t sodium dichromate and 0.66 t anhydrous sodium sulfate, the following materials and utilities are required.

Chromite ore	1.1 t	Fuel oil	0.52 t
Limestone	1.65 t	Steam	3 t
Soda ash	0.88 t	Electricity	1980 MJ
Sulfuric acid, 66°Bé	0.5 t	Direct labor	15 work-h

Fig. 5.7. Flowchart for the manufacture of sodium dichromate from chrome ore.

erally results in an excellent product whiteness, with little or no *deterioration* of the organic matter that is bleached. Organic applications include manufacture of epoxides and glycols from unsaturated petroleum hydrocarbons, terpenes, and natural fatty oils. The resultant products are valuable plasticizers, stabilizers, diluents, and solvents for vinyl plastics and protective-coating formulations. The 90 to 100% concentrations represent a self-centered energy source which leaves no residue or corrosive gas, ideal for specialized propulsion units for aircraft, missiles, torpedos, and submarines. New uses are as a source of oxygen in municipal and industrial wastewater treatment systems and as an oxidant for in-place solution mining of low-grade uranium ores.

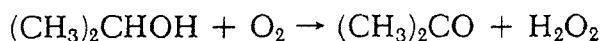
MANUFACTURE.³⁴ All hydrogen peroxide manufacturing plants built since 1957 utilize the autooxidation of an anthraquinone. The quinone is hydrogenated to the hydroquinone using either Raney nickel or palladium as a catalyst. Subsequent oxidation with air produces hydrogen peroxide and regenerates the quinone. The reactions can be illustrated with the easily oxidizable 2-ethylantraquinone.



The hydrogen peroxide is water-extracted and concentrated, and the quinone is recycled for reconversion to the hydroquinone. A second organic process uses liquid isopropyl alcohol,

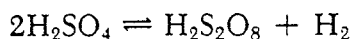
³⁴Du Pont Innovation 5 (1) 5 (1973); ECT, 3d ed., vol. 13, 1981, p. 12.

which is oxidized at moderate temperatures and pressures to hydrogen peroxide and an acetone coproduct:

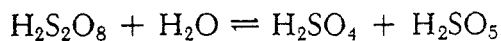


After distillation of the acetone and unreacted alcohol, the residual hydrogen peroxide is concentrated.

An older electrolytic process produced hydrogen peroxide by the anodic oxidation of sulfate radicals to form peroxydisulfate intermediates.³⁵ Sulfuric acid electrolyte has low current efficiency (70 to 75 percent), but the use of ammonium sulfate causes crystallization problems, so a mixture is used to obtain a current efficiency of 80 percent or higher and yet not block the cell with crystal formation. The electrolyte is fed into a typical cell held at 35°C or below with platinum metal for the anode:



The cell product, i.e., the persalt, or peracid, and sulfuric acid in water are subjected to hydrolyses at 60 to 100°C to yield hydrogen peroxide, as shown by the following simplified reactions:



The electrolytic process requires that the electrolyte be continuously purified and also has very high capital and power requirements. Thus it cannot economically compete with the anthraquinone oxidation process.

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³⁵ *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 6, McGraw-Hill, New York, 1982, p. 747.

Chapter 6

Explosives, Propellants, and Toxic Chemical Agents

Many professional chemists and chemical engineers tend to view the subject of explosives and propellants from observation of their end-use effects, which are frequently spectacular and dramatic. Explosive manufacture is a constantly changing and growing field that greatly needs innovative professionals. The usual unit operations are applied here with new and frequently difficult constraints because of the nature of the products. Continuous processes are replacing batch ones for nitration, emulsification, and gelation with improved uniformity of product and lower cost. Recent advances in computer-controlled processing have found many applications in manufacturing. Commercial explosives are essential to such industries as mining and quarrying, construction, geophysical exploration, and metal cutting and forming. Major engineering jobs such as the construction of tunnels and dams would be impossibly expensive without explosives. Table 22.1 summarizes U.S. consumption of explosives.

HISTORY AND ECONOMICS. An explosive mixture of sulfur, charcoal, and saltpeter, called black powder, was known to the Chinese centuries ago; its use in propelling missiles was demonstrated shortly after 1300. The discoveries of nitroglycerine and nitrocellulose shortly before 1850, and the invention of dynamites and the mercury fulminate blasting cap soon after, were epochal events of the high-explosives era. Smokeless powder was first made in 1867. The demand for more powerful and uniform propellants for the space program offered a recent, new challenge. In times of war, increased quantities are required; for example, roughly 3×10^9 kg was manufactured in the United States between January 1940 and V-J day. Industrial and commercial use is very substantial: 1.6×10^9 kg/year in 1982. Although a great many compounds and mixtures are explosive, comparatively few of them are suitable for explosive use because of the critical restrictions on stability, safety, and price. Most explosive compounds are too expensive and too sensitive for much use.

TYPES OF EXPLOSIVES

An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of a great deal of heat and much gas. The hot gases cause extremely high pressure if the explosive is set off in a confined space. Explo-

Table 6.1 U.S. Industrial Consumption of Explosives
(in thousands of metric tons)

	1977	1978	1979	1980
Coal mining	952	986	1017	1138
Metal mining	203	261	279	254
Quarrying and nonmetal mining	238	275	297	284
Construction work and other uses	<u>294</u>	<u>264</u>	<u>267</u>	<u>267</u>
Total industrial	1687	1786	1860	1943

SOURCE: *Minerals Yearbook*, U.S. Bureau of Mines, 1982.

sives differ widely in their sensitivity and power. Only those of a comparatively insensitive nature, capable of being controlled and having a high energy content are of importance industrially or militarily. There are three fundamental types of explosives: mechanical, atomic, and chemical. This chapter is about chemical explosives. For purposes of classification it is convenient to place chemical explosives in two divisions in accordance with their behavior.

1. Detonating, or high, explosives. (a) Primary, or initiating, explosives (detonators); (b) booster and secondary explosives.

2. Deflagrating, or low, explosives.

There exists a very great difference between the detonating and deflagrating explosive types. High explosives detonate at very high rates, from 2 to 9×10^3 m/s, and the reaction front is a shock phenomenon moving actively throughout the material. Low explosives, or propellants, burn in layers parallel to the surface at low rates, around 10^{-2} m/s, and the reaction front is a flame.

Cook¹ lists the major explosive chemicals according to military or commercial use. Variations in their blasting characteristics are obtained by (1) altering physical conditions such as density and granulation and (2) combining ingredients—paraffin, aluminum, and waxes, for example. A table of nonexplosive additives appears in the same reference.

INITIATING, OR PRIMARY, EXPLOSIVES. Initiating, or primary, explosives are materials that are quite shock and heat sensitive and that can be made to explode by the application of a spark, flame, friction, or heat source of appropriate magnitude. They are very dangerous to handle and are used in comparatively small quantities to start the explosion of larger quantities of less sensitive explosives. Initiating explosives are generally used in primers, detonators, and percussion caps. They are usually inorganic salts, whereas booster and other high explosives and many conventional propellants are largely organic materials.

Primary explosives used include mercury fulminate [$\text{Hg}(\text{ONC})_2$], lead azide $\text{Pb}(\text{N}_3)_2$, basic lead styphnate (trinitroresorcinate), diazodinitrophenol, and tetrazine (a complex conjugated nitrogen compound). Most priming compositions consist of mixtures of primary explosives, fuels, and oxidants. An example is 15% antimony sulfide, 20% lead azide, 40% basic lead styphnate, 20% barium nitrate, and 5% tetrazine. Glue, which acts as a binder, and ground glass, which increases internal friction, may be added.

¹Cook, *Science of High Explosives*, ACS Monograph 139, Reinhold, New York, 1958, p. 4.; also Riegel, *Industrial Chemistry*, 7th ed., Reinhold, New York, 1974, pp. 676–683, this contains an extensive list, together with characteristics and uses.